



Admittance Analysis of Proton conducting polymer electrolyte PVA:NH₄PF₆:ZrO₂

Dr. (Mrs) K.P.Radha

Associate Professor of Physics, S.F.R. College for Women, Sivakasi, Tamilnadu.

ABSTRACT

Proton conducting composite polymer electrolyte based on Poly vinyl alcohol (PVA) and ammonium hexafluoro phosphate (NH₄PF₆) complex with different molar ratios of the nanofiller Zirconium di oxide ZrO₂ have been prepared by Solution Casting technique. Concentration dependent Conductivity reveals that the polymer electrolyte 70PVA:30NH₄PF₆:2ZrO₂ has the maximum ionic conductivity (2.5688x10⁻³ Scm⁻¹) with minimum activation energy (0.123883 eV) at ambient temperature. The spectroscopic plot of Y'' represents the bulk element in series with electrode capacitance. The frequency independent region in the spectroscopic plot of Y' indicates the accumulation of the charge carriers near the electrode.

KEYWORDS

AC impedance analysis, admittance, dielectric

Introduction:

One way of enhancing the conductivity of polymer electrolytes without significantly compromising their mechanical properties is via the incorporation of the nanofiller ZrO₂, TiO₂, Al₂O₃, SiO₂ or solid plasticizers. These plasticizers impart the dual advantages of increasing local segmental mobility in the polymer chains reflected in decreasing glass transition temperature (T_g) and increasing the degree of dissociation of the salt [1]. When the dielectric constant of the solid plasticizer is greater than that of the polymer host the addition of such plasticizer will increase the permittivity of the mixture. Effectively solid plasticizers may serve to promote both the number of available charge carriers and their mobility through the polymer network.

In our earlier work, we have dealt with preparation of polymer electrolyte with PVA and ammonium hexafluoro phosphate (NH₄PF₆). In the present work, the optimized high conductivity polymer electrolyte 70PVA:30 NH₄PF₆ (mol %) has been further optimized to find the effect of the nanofiller ZrO₂ of 45nm size on the ionic conductivity of the proton conducting polymer electrolyte.

Experimental:

Preparation

Poly (vinyl alcohol) (PVA) with molecular weight 1,25,000 (AR grade Sd fine chem. make), ammonium hexafluoro phosphate (NH₄PF₆) purchased from Aldrich, USA and the nano filler Zirconium di Oxide (ZrO₂) from Aldrich USA of particle size 45nm and Dimethyl Sulphoxide (DMSO) as solvent are used as starting material to prepare composite polymer electrolytes by solution casting technique. From our earlier work, it has been observed the optimum concentration of PVA and NH₄PF₆ as 70mol% and 30mol%. The nano filler ZrO₂ is added to this optimum concentration (70PVA:30 NH₄PF₆) as 1mol%, 2mol% and 3mol%. Appropriate weights of PVA, NH₄PF₆ are dissolved in DMSO by using magnetic stirrer. The Nano filler ZrO₂ is suspended in the solution and then stirred well to get homogenous mixture. The mixture is then poured into glass Petri dish and is allowed to evaporate the solvent in the vacuum oven at 80°C for 5 days. Free standing nature of the electrolyte has obtained.

Conductivity measurements:

AC conductivity measurements have been carried out on PVA - NH₄PF₆ systems of uniform thickness having an area of 1 cm². Polymer electrolytes have been sandwiched between two stainless steel (SS) electrodes applying a potential of 1V from 42 Hz to 1 MHz using HIOKI make LCZ meter (model 3532) interfaced to a computer. The conductivity has been

calculated from complex impedance plots of measured impedance (Z) and phase angle (θ). The temperature of the cell has been controlled using a thermostat and electrical measurements of the polymer electrolytes have been carried out in the temperature range 303K – 343K.

Results and discussion:

Concentration dependent conductivity

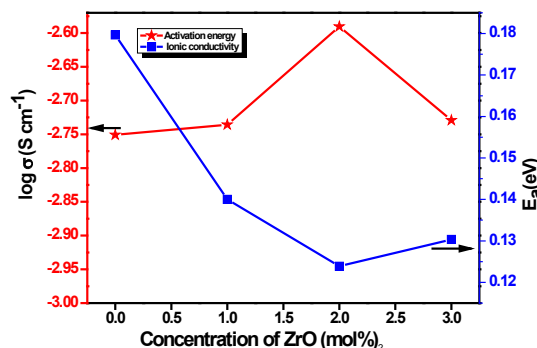


Figure 1 Variation of conductivity and activation energy of 70 PVA: 30 NH₄PF₆ as a function of ZrO₂ concentration at 303K.

The activation energy of the composite polymer electrolyte decreases with increase in the ionic conductivity as shown in Fig-1. Since the proton ion transfer is greatly affected by the polymer segmental motion, a composite electrolyte with lower activation energy suggests rapid ion conduction and hence higher conductivity [2]. Normally ionic conductivity of the polymer electrolyte depends upon both charge carrier concentration, n and carrier mobility μ as

$$\sigma = nq\mu$$

where q representing the charge of mobile carrier. The charge carrier concentration n depends upon both the dissociation energy U involved and dielectric constant ϵ as

$$n = n^0 \exp(-U/\epsilon kT)$$

Where k is Boltzmann constant and T the absolute temperature. Upon incorporation of the nanofiller ZrO₂ to the electrolyte 70 PVA:30 NH₄PF₆ dielectric constant has been experimentally found to increase during measurements (Fig-2). It

means that the increase in the dielectric constant would lead to increase in value of n which in turn enhances the ionic conductivity. The polymer electrolyte 70PVA:30NH₄PF₆:2ZrO₂ has the maximum ionic conductivity (2.5688x10⁻³ Scm⁻¹) with minimum activation energy (0.123883 eV). The minimum activation energy indicates that there is decrease in the energy carrier for proton ion transport in the polymer matrix.

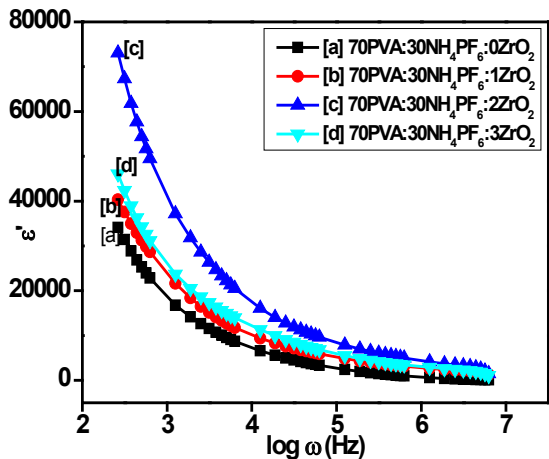


Figure 2 Dielectric constant of all composite polymer electrolytes at 303K

There is decline in the ionic conductivity for 3 mol% of nanofiller ZrO₂ incorporated composite polymer electrolyte. The reason may be that the distance between dissociated ion may become too close and they are able to recombine and form neutral ion pairs which do not contribute toward conductivity [3].

Admittance analysis:

The admittance plot is a powerful method to investigate the ion conduction mechanism. The complex admittance Y* is given by the relation

$$Y^* = 1/Z^* = Y' + j Y''$$

where Y' and Y'' is the real and imaginary part of admittance respectively. The variation of Imaginary part of admittance as a function of frequency of the best conducting electrolyte at different temperatures has been depicted in Fig 3. The Imaginary part of admittance curve increases with increase in frequency, reaches maximum and then decreases. The presence of peak indicates that there is series combination of resistance (R_b) and capacitor (C_e). The spectroscopic plot of Y'' represents the bulk element in series with electrode capacitance as shown in the equivalent circuit-1.

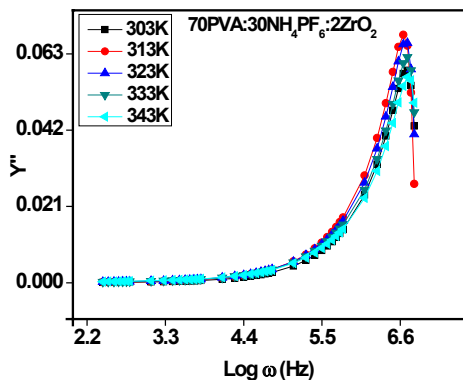
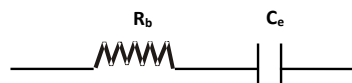


Figure 3 Imaginary part of admittance as a function of frequency of the best conducting electrolyte at different temperatures

Equivalent Circuit - 1



The bulk resistance (R_b) can be obtained from the relation

$$Y'' = 1/2R_b$$

Using the bulk resistance, ionic conductivity of the samples can be calculated by the relation

$$\sigma = l/R_b A$$

where l is the thickness of the polymer electrolyte and A is the surface area of the electrolyte.

Table 1 Ionic Conductivity values of PVA:NH₄PF₆:2ZrO₂ polymer electrolyte at different temperatures

Composition 70PVA:30NH ₄ PF ₆ :2ZrO ₂	Ionic conductivity (Scm ⁻¹)
303	2.5688 x10 ⁻³
323	3.0429x10 ⁻³
343	3.1404x10 ⁻³

It has been observed that the peak maximum of imaginary component (y'') of the admittance as a function of frequency increases with increase in temperature. The reason may be that there is increase in capacitance due to the accumulation of charges at the electrode – electrolyte interface [4]. The frequency corresponding to peak maximum varies with temperature T according to

$$\omega_p = \omega_s \exp(-E_a/kT)$$

where ω_s is the pre exponential factor E_a is the activation energy and k is the Boltzmann constant. The conductivity relaxation time of the sample at various temperature can be calculated from the relation.

$$\tau = \frac{1}{\omega_{max}}$$

The conductivity relaxation time of the best conducting electrolyte is 2.44 x10⁻⁶ s. From the table, it has been observed that the ionic conductivity of the electrolyte increases with temperature. It suggests the temperature dependence of the ionic conductivity.

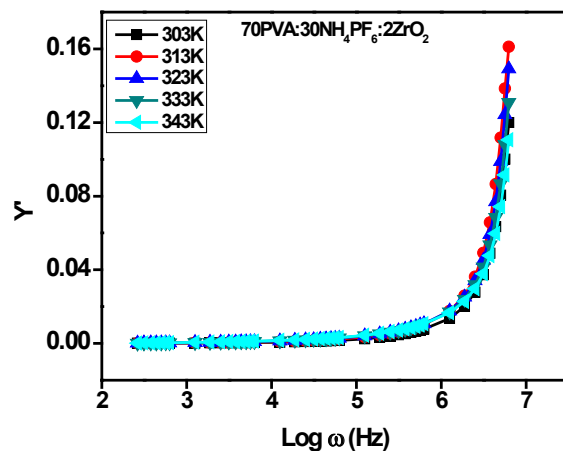


Figure 4 Real part of Admittance (Y') vs frequency plot of best conducting composite polymer electrolyte at different temperatures.

The plot between real part of the admittance and frequency is useful to diagonalise the conduction mechanism (Fig 4). The frequency independent region indicates the accumulation of the charge carriers near the electrode [5].

Conclusion:

The composite polymer electrolyte of PVA:NH₄PF₆:XZrO₂ (X = 0,1,2,3 in mol%) have been prepared by Solution Casting technique

The polymer electrolyte 70PVA:30NH₄PF₆:2ZrO₂ has the maximum ionic conductivity (2.5688x10⁻³ S cm⁻¹) with minimum activation energy (0.123883 eV).

The presence of the peak in the imaginary part of the admittance suggests that there is series combination of resistance (R_b) and capacitor (C_o).

From the dielectric analysis it has been observed that the incorporation of the nanofiller ZrO₂ enhances the dielectric constant of the composite polymer electrolytes.

References:

1. L. Yang, J.Lin, Z. Wang, C. Wang, R. Zhou, Q.Liu, Solid State Ionics 40/41 (1990) 616.
2. T .Winie, S. Ramesh, A.K.Arof , Physica B,404 (2009) 4308.
3. Y.M. Yusof, H.A. Illias, M.F.Z. Kadir, Ionics 20 (2014) 1235.
4. C.S.Ramya, S.Selvasekarapandian, G.Hirankumar, T.Savitha, P.C.Angelo J.Non – Cryst. Solids 354 (2008) 1494.
5. 2011 International conference on environment and Industrial Innovation IPC-BEE 12 (2011) 70.